High Aluminum Wastes: Sludge Feed Preparation and Implications on Vitrification

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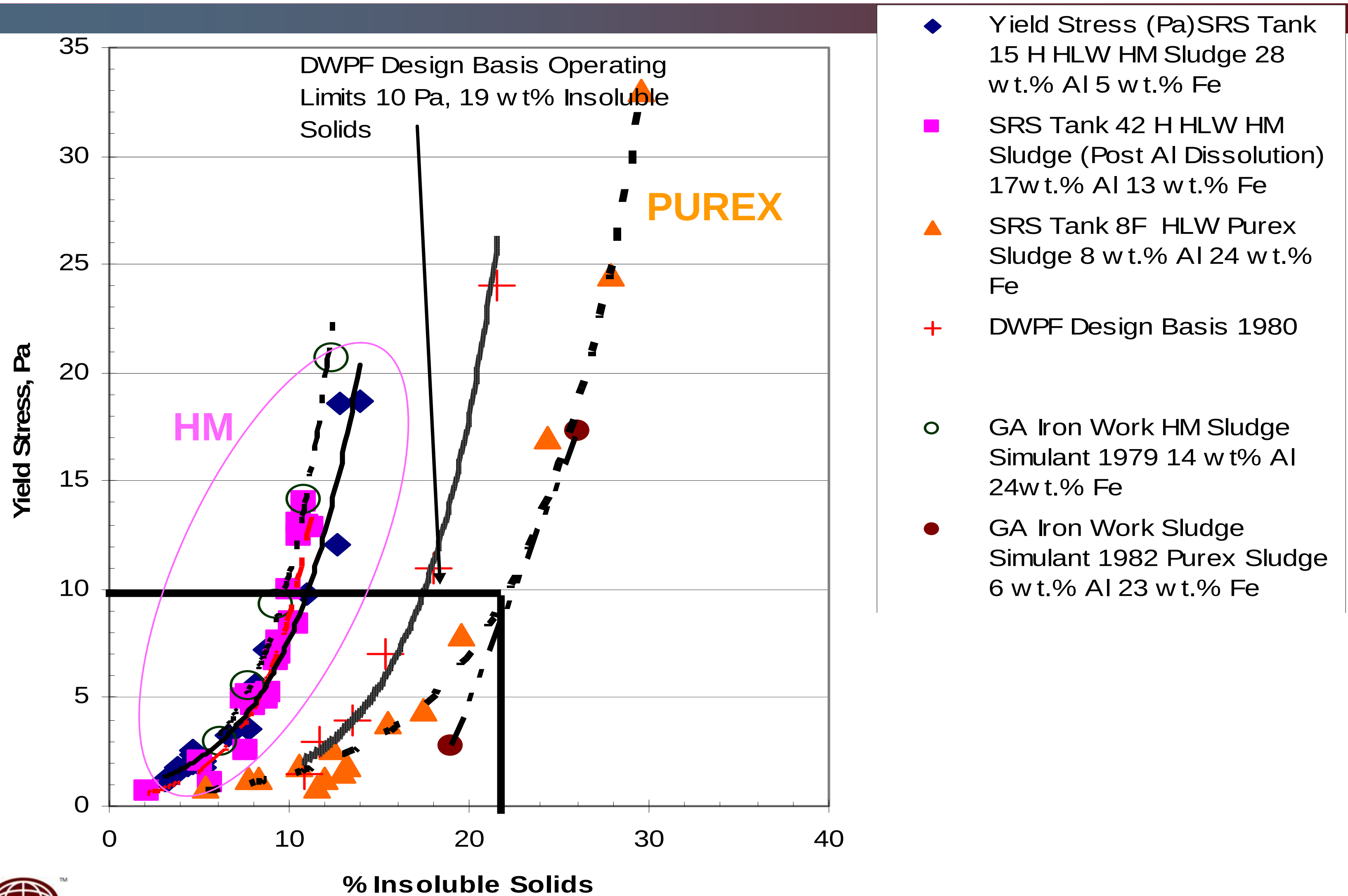
Outline

- Al-dissolution considerations and/or impacts to:
  - Slurry Rheology
  - Material Settling and Transfer Considerations
  - Glass Formulation
    - Based on DWPF and EM-21 Studies
      - Al_2O_3 solubility
      - Nepheline formation
      - Waste loading
      - Melt rate
      - Waste throughput
  - Thoughts or considerations on implementation

Slurry Rheology Issues

- Physical limitations or criteria are defined based on yield stress
  - Tank Farm limits and targets
    - 5 Pa and 12-15 wt% insoluble solids for F to H area transfers
    - 5 Pa target for H-area transfers
  - Current DWPF design basis (operating limits):
    - 10 Pa and 19 wt% insoluble solids
- Significant differences observed in rheological behavior between Purex and HM based sludges as a function of % insoluble solids
  - HM based feeds show an exponential increase in yield stress at lower % insoluble solids as compared to Purex based feeds
    - appears to be independent of Al-dissolution

Sludge Rheology Issues



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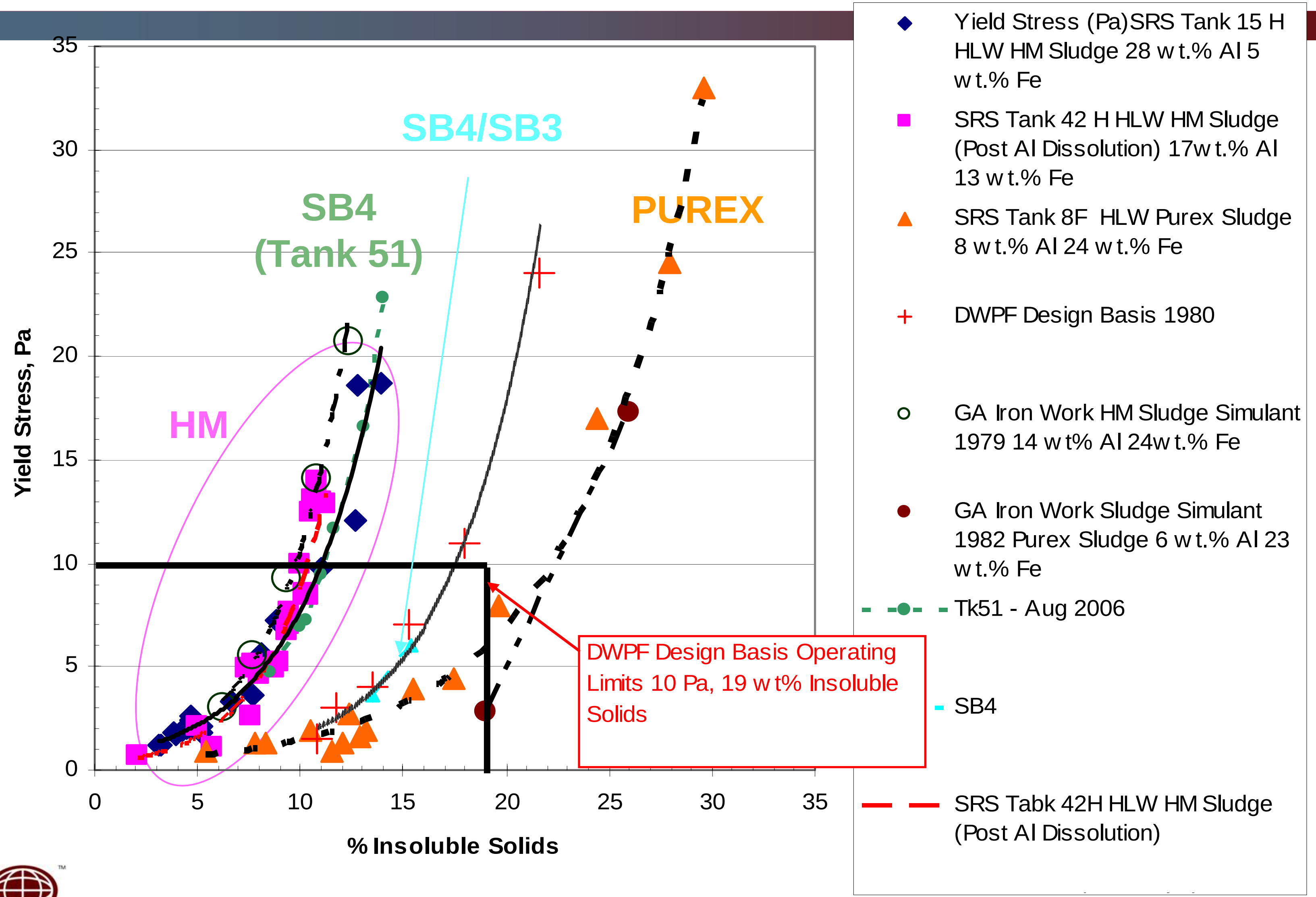
Sludge Rheology Issues



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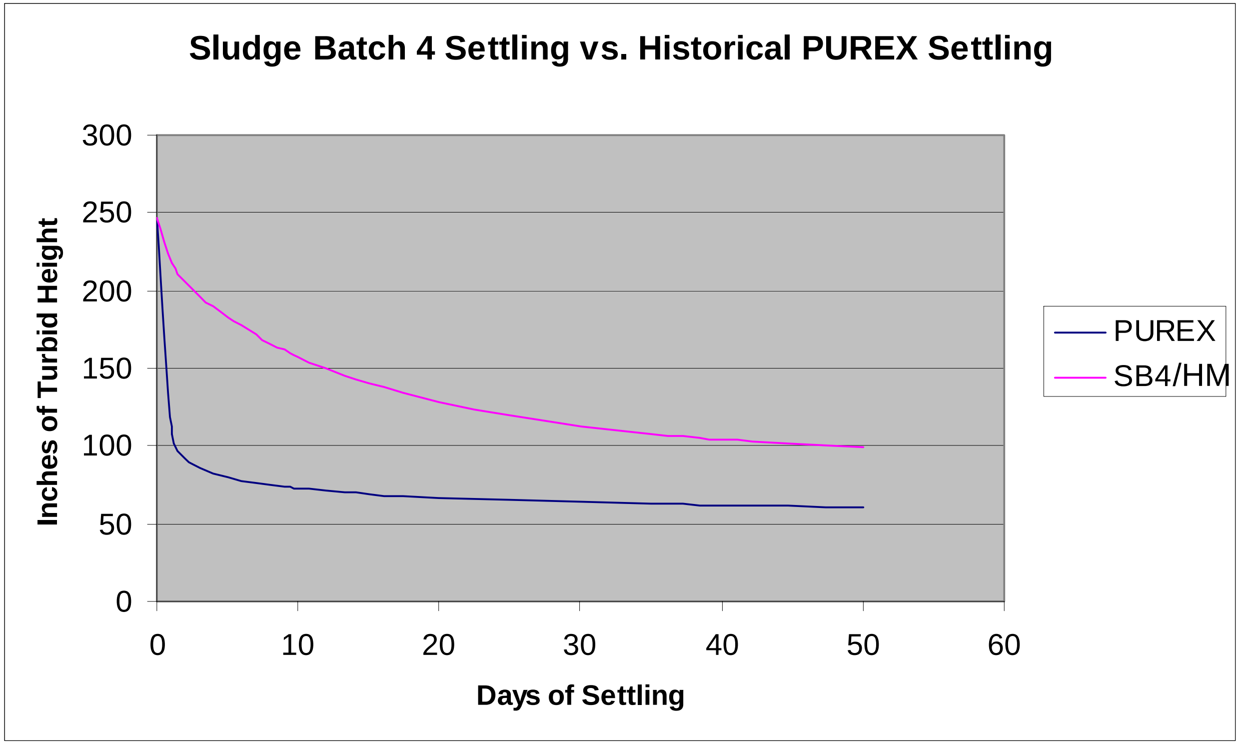
Sludge Rheology Issues

- HM-based sludges appear to provide more physical limitations
  – Dependent on blending and washing strategy to control
- Recent rheological measurements on Sludge Batch 4 (SB4) confirmed high yield stress
  – When SB4 blended with SB3 (70/30 and 60/40), sludge characteristics were more favorable (as shown in previous slide)
  – "Over" washing sludge (removal of salts) negatively impacted rheology of feed
    - Can occur even with PUREX type feeds, SB2 example

Sludge Settling Comparison: HM vs PUREX



If settling time >> quiescent time smaller batches will be required

- Impact of slower settling times
  - Quiescent time; hydrogen retention
  - Sludge preparation time
- Slow settling has the potential to prevent wash/ concentration endpoints from being met

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Glass Formulation Issues

- Current R&D for high Al_2O_3 based feeds
  - DWPF glass formulation
    - Primarily SB4
      - HM-based, no Al-dissolution
  - EM-21 International Program
    - Evaluating both DWPF and Hanford compositional regions
- Primary issues being addressed:
  - Al_2O_3 solubility
  - Nepheline formation
    - Impact of high B_2O_3 on nepheline formation
  - Waste loading (impact on projected operating windows)
  - Melt rate

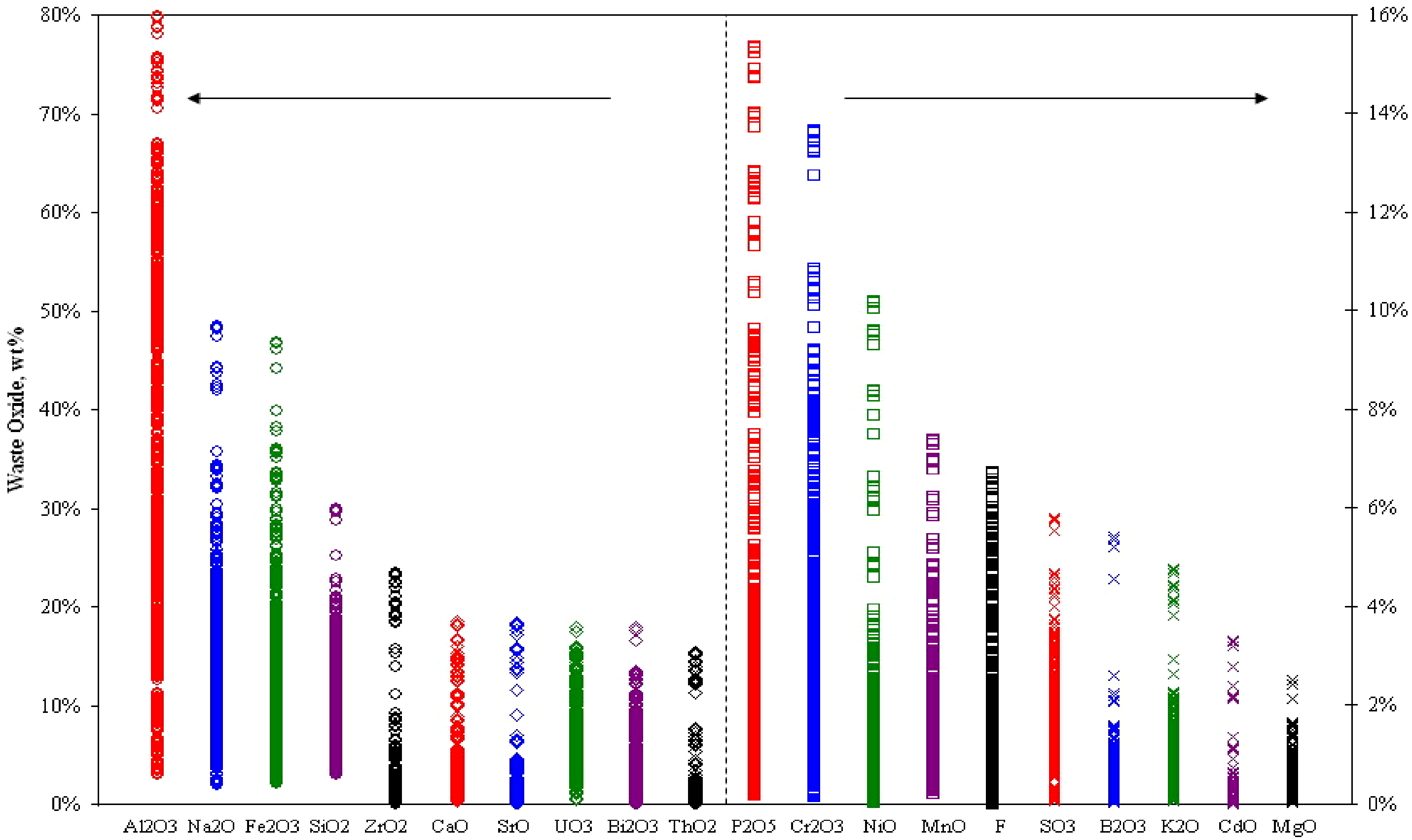
Al_2O_3 Projections in Sludge

- Significant difference in projected Al_2O_3 concentrations between DWPF and Hanford sludges
  - DWPF Al_2O_3 concentrations (without Al-dissolution) are on the order of 25 – 45 wt% in sludge (current projections)
    - Projections based on current blending scenarios
    - SB4 Al_2O_3 projections are ~ 25 – 30 wt%
  - Hanford projections indicate Al_2O_3 concentrations up to ~80 wt% are possible
    - High Na_2O concentrations (up to ~50 wt%) also projected in Hanford waste

SB4 Compositional Projections

	Case 1 (30/70 Blend)			Case 2 (40/60 Blend)		SB4 Blend
	SB4 Batch	SB4 Blend		SB4 Batch	SB4 Blend	10-10-06 Composition
	Wt % Oxide, Calcine Basis	Wt % Oxide, Calcine Basis		Wt % Oxide, Calcine Basis	Wt % Oxide, Calcine Basis	(Served as the basis for VS w Frit 418) Wt % Oxide, Calcine Basis
Al_2O_3	42.46	26.09		42.84	28.19	25.49
CaO	1.45	2.75		1.46	2.55	2.77
Cr_2O_3	0.12	0.20		0.12	0.19	0.20
Fe_2O_3	15.69	28.89		15.84	26.82	28.99
MgO	0.67	2.74		0.68	2.43	2.77
MnO	3.37	5.77		3.40	5.39	5.78
Na_2O	29.60	18.33		28.95	20.40	18.71
NiO	1.17	1.66		1.18	1.58	1.66
SO_4	0.00	0.87		0.00	0.87	0.87
SiO_2	1.24	2.70		1.26	2.47	2.71
U_3O_8	2.87	8.95		2.89	8.03	9.03

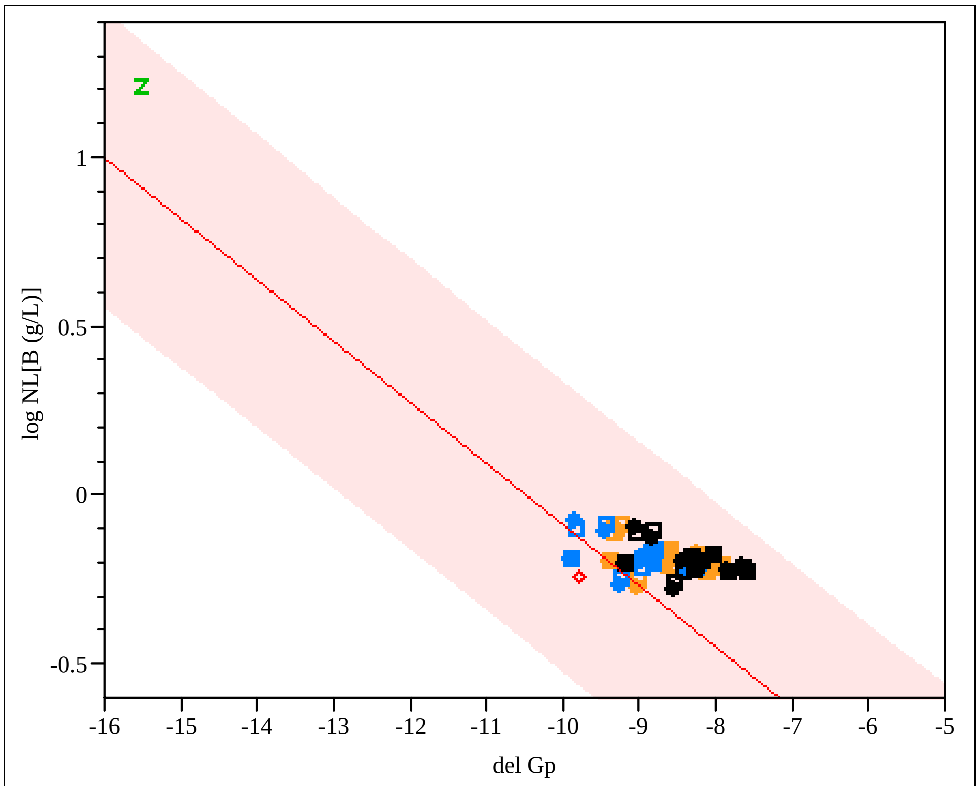
Al_2O_3 Projections in Sludge: Hanford



SB4 Glass Formulation Efforts

- Al_2O_3 solubility in glass
  - SB4's Al_2O_3 concentration: ~ 28%
  - At 45% waste loading, Al_2O_3 concentrations in glass projected to be ~11%
    - Al_2O_3 solubility in glass not an issue at this level
    - SB4 studies have fabricated multiple glasses ranging from 9 – 12 wt% Al_2O_3
      - Complete dissolution of Al_2O_3 in glass
      - Acceptable in terms of process and product performance constraints
    - EM-21 task has successfully incorporated up to 27% Al_2O_3 in glass
      - higher Al_2O_3 concentrations targeted given Hanford projections

Frit 418 – SB4 Variability Study



		Sludge	Heat Treatment	Composition
	1	ARM		reference
	2	EA		reference
	3	SB4VS	ccc	measured
	4	SB4VS	ccc	measured bc
	5	SB4VS	ccc	targeted
	6	SB4VS	quenched	measured
	7	SB4VS	quenched	measured bc
	8	SB4VS	quenched	targeted

- Highest release: 0.84 g/L
  - SB4VS-43ccc
    - ~9.9% Al_2O_3 in glass
- EA glass: 16.695 g/L
- SB4VS-38ccc (10.5% Al_2O_3)
  - NL [B]: 0.63 g/L

SB4 Glass Formulation Efforts

- Nepheline formation
  - A crystalline phase that can have negative impact on the durability of the glass
  - Nepheline discriminator:

$$\frac{SiO_2}{SiO_2 + Na_2O + Al_2O_3} > 0.62$$

  - Glasses with values less than 0.62 prone to nepheline formation
  - Known that B_2O_3 suppresses nepheline formation
    - No B_2O_3 term in the discriminator function → current R&D addressing issues (DWPF and EM-21 International programs)
    - Potential impact of nepheline discriminator ….. artificially cut-off compositional regions of interest (higher Al_2O_3 concentrations)

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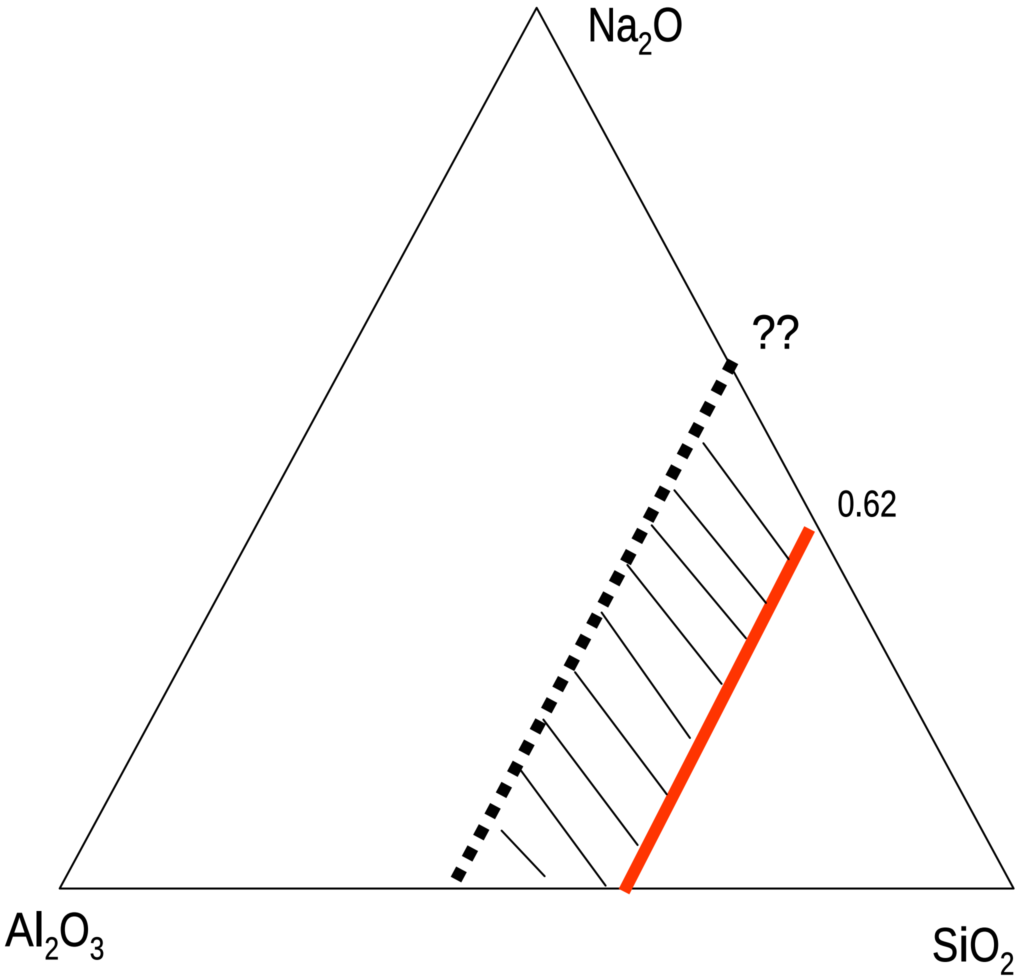
Nepheline Discriminator: Adjustment?



- EM-21 task has fabricated glasses with nepheline discriminators < 0.45
  - Al_2O_3 concentrations between 18 – 27% in glass (high B_2O_3)
  - Preliminary assessments indicate acceptable glass durabilities
- DWPF and EM-21 tasks integrated to re-evaluate discriminator
  - Remove conservatism

Impact on Waste Loading

- For DWPF:
  - Strategic frit development efforts for SB4 have mitigated the potential negative impacts of higher Al_2O_3 concentrations
    - Al_2O_3 solubility not an issue
    - Higher B_2O_3 based frits developed to suppress nepheline formation
    - SB4 glass systems or projected operating windows are limited by other process related criteria
      - Liquidus temperature
      - Low viscosity
        - » Avoid being nepheline limited → product quality constraint

SB4 Projected Operating Windows

Nepheline limited

Preferred: using assumptions of high B and Na for melt rate

500 series: higher B_2O_3 contents

Frit ID	B_2O_3 (in frit)	Na_2O (in frit)	Case 1 (30/70)	Case 2 (40/60)	"Average" (~35/65)
418	8	8	25 – 42 T_L	25 – 43 Neph	25 – 43 T_L
425	8	10	25 – 43 Neph	25 – 41 Neph	25 – 42 Neph
503	14	4	25 – 37 T_L	25 – 40 T_L	25 – 38 T_L
503-m1	14	5	25 – 38 T_L	25 – 41 T_L	25 – 39 T_L
505	14	6	25 – 39 T_L	25 – 42 T_L	25 – 41 T_L
503-m2	14	7	25 – 40 T_L	25 – 42 Neph	25 – 42 T_L
503-m3	14	8	25 – 41 T_L	25 – 41 Neph	25 – 42 Neph
503-m4	14	9	25 – 42 T_L /Neph	25 – 40 Neph	25 – 41 Neph
503-m5	14	10	25 – 39 low η	25 – 38 low η/Neph	25 – 38 low η
503-m6	16	8	25 – 41 T_L	25 – 40 Neph	25 – 41 low η/Neph

NOTE: Operating windows defined by model predictions (no input on melt rate); "optimum" waste throughput may not be at maximum waste loading

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Melt Rate for SB4

- Preliminary assessments indicated a significant decrease in melt rate between SB3 and SB4 based systems without frit composition changes
  - Frit 418 – SB3 versus Frit 418 – SB4
    - ~20 – 30% reduction in melt rate for SB4 system
- Strategic frit development efforts have resulted in higher melt rates relative to Frit 418
  - Slurry fed melt rate tests indicated:
    - Frit 503 has the potential to provide comparable melt rates to the Frit 418 – SB3 system
    - Higher B_2O_3 based frits have:
      - Suppressed nepheline formation and led to higher melt rates

Other Issues or Thoughts

- How much Al to remove?
  - DWPF has a lower Al_2O_3 limit as a part of the SME acceptability criteria (e.g., > 4% Al_2O_3 in glass or > 3 wt% with a upper alkali constraint)
    - If pretreatment efforts remove too much Al_2O_3 from sludge, Al_2O_3 would have to be added back through the frit to meet criterion……
  - Al_2O_3 in glass is a function of Al_2O_3 in sludge and waste loading range of interest
    - must cover a range of waste loadings
      - If lower WL needed for max throughput, need to ensure Al_2O_3 concentration in glass is met
- Melt rate differences between boehmite and gibbsite?
  - Understanding that Al-dissolution is effective in removing gibbsite…..
    - Is there a disadvantage in melt rate by removing gibbsite?
    - Does Gibbsite convert to boehmite in cold cap?

Other Issues or Thoughts

- Impact of Al-dissolution on salt stone?
  - Set or gel times?
- Impact of Al-dissolution on mass reduction?
  - Obviously there is a positive effect of Al-dissolution in terms of mass reduction
    - Is there an optimum point at which further removal does not improve the overall flowsheet and waste throughput for DWPF or the HLW system in general?
    - Cost benefit analysis?

To Implement or Not (Degree of Implementation)?

- There are a number of issues associated with the decision to perform Al-dissolution including:
  - Sludge settling issues
  - Rheological issues
  - Glass formulation issues
    - For DWPF:
      - Al_2O_3 solubility does not appear to be an issue
      - Higher B_2O_3 frits have suppressed nepheline formation and yielded higher melt rates
        - » Melt rates and waste throughputs to be monitored once SB4 is processed in DWPF to confirm laboratory results
      - Projected operating windows not dictated by Al_2O_3 based issues

To Implement or Not (Degree of Implementation)?

- An integrated assessment of the impacts of Al-dissolution should be made:
  - To meet mass reduction needs, how far should Al-dissolution be executed?
    - DWPF and Hanford answers could be different?
  - If Al-dissolution reduces mass but causes processing issues in the facility (e.g., rheology), is waste throughput maximized?
  - Al-dissolution for DWPF should not be implemented to the extent where Al_2O_3 would need to be added to the frit?
  - Is there an optimum point at which further removal does not improve the overall flowsheet and waste throughput for DWPF?
    - Cost benefit analysis for overall HLW system or flowsheet?